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P. J. Photinos [a] & A. Saupe [a]
[a] Liquid Crystal Institute and Department of Physics, Kent State University, Kent, Ohio, 44242
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Model Calculations on the Electric Conductivity of the N_c Phase

P. J. PHOTINOS and A. SAUPE

Liquid Crystal Institute and Department of Physics, Kent State University, Kent, Ohio 44242

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A theoretical study of the electric conductivity of a system consisting of a body-centered tetragonal lattice of insulating cylinders, embedded in a uniform and isotropic conducting medium is presented. The model is described by three parameters: the volume fraction occupied by the cylinders (here taken to be less than 50%); the diameter to length ratio of the cylinders, d/l; and the ratio of the minimum distances between cylinders normal and parallel to the cylinder axis, ξ.

We find that the conductivity anisotropy is in general smaller than the value corresponding to infinitely long cylinders. The anisotropy can assume both positive and negative values. The sign is largely determined by the ratio ξ.

The usefulness of the model in relation to the N_c lyotropic mesophase is discussed.

INTRODUCTION

The evaluation of the electric conductivity of heterogeneous systems with periodic structure has been the subject of numerous papers, dating back to Maxwell, and a number of approximate expressions for the principal values of the conductivity are known, which are of interest to various systems.

In connection with lyotropic mesophases, Francois[1] first examined a hexagonal arrangement of infinitely long cylinders, and derived approximate expressions for the conductivity at high volume concentration of cylinders. These expressions were then used to interpret measurements on unoriented middle soap systems (hexagonal phase).

More recently, we presented numerical calculations on the conductivity of the hexagonal phase[2] and the N_L phase.[3] In the latter case we also discussed the usefulness of such calculations (in conjunction with conduc-

tivity measurements on oriented samples[2]) in assessing the size of the disc-like aggregates of the N_L phase.

In the present work we examine the N_c lyotropic mesophase, which is a nematic phase characterized by cylindrical aggregates.

THE MODEL

Although the spatial arrangement of the cylindrical aggregates in the N_c phase lacks any translational long-range order, we will assume for mathematical convenience, a lattice structure. More specifically, we will assume that the cylindrical aggregates are rigid, and that their centers are arranged on a body-centered tetragonal lattice. The cylinder axes are oriented parallel to the z-axis. Projections of the arrangement on the xy and the xz planes are shown in Figure 1.

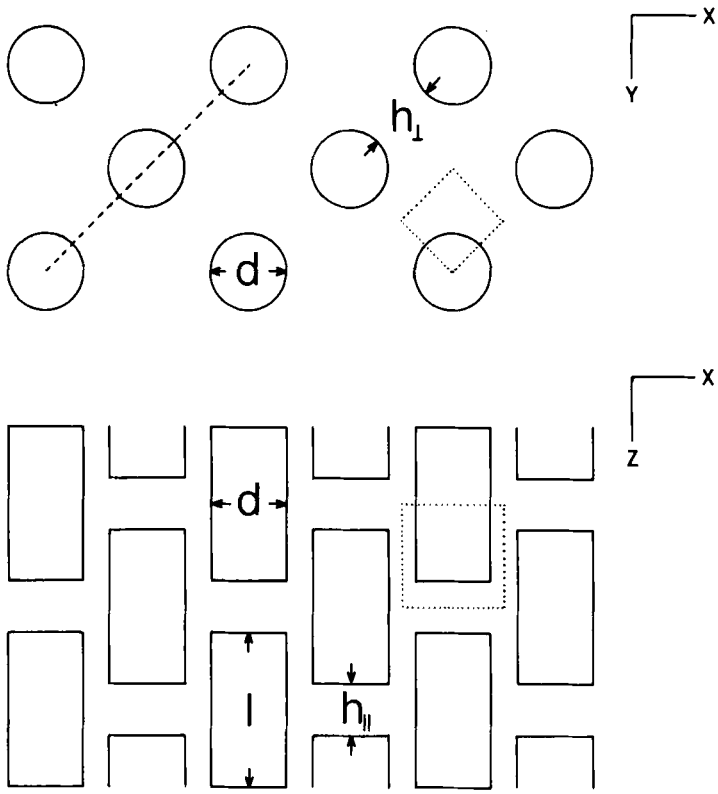

FIGURE 1 xy and xz projections of the tetragonal body-centered lattice.

The remaining assumptions relate to the conduction mechanism, namely, that the cylinders are insulating, and that the interstitial water phase is conducting uniformly and isotropically.

At this point it is convenient to introduce some parameters pertaining to the structure. Referring to Figure 1, d is the diameter of the cylinders and l is their height. $h_\perp$ is the distance between surfaces of two nearest neighbors on the xy projection, and $h_\parallel$ is the distance between nearest neighbors along the z-axis. v is the fraction of the total volume that is occupied by the cylinders (the concentration by volume), and ξ is the ratio $h_\perp/h_\parallel$.

Apart from an overall scaling factor, the structure is described completely by three parameters. Here we choose v, the ratio d/l and ξ.

The calculations were carried out for $v = 0.1$, 0.2, 0.3, and 0.4, thus covering a concentration range of practical interest in connection with lyotropic mesophases. Since the aggregates in the N_c phase are elongated, the interesting range for the ratio d/l is below unity. For mathematical convenience we used the value $d/l = 0.1$ as the lower limit. As for the parameter ξ, we note that the large values lead to the infinitely long cylinder model. On the other hand ξ cannot be very small, as this is not allowed by the lateral repulsive forces between cylinders. Here we choose for ξ the range 0.2 to 3.0.

The components of the conductivity can be evaluated by first solving Laplace's equation with the appropriate boundary conditions, for each principal axis. In view of the symmetry of the arrangement, it is sufficient to consider a cell containing one quadrant of half length of a cylinder, as indicated by the dotted lines in Figure 1. In the numerical calculations we used the procedures outlined in Ref. 3.

RESULTS AND DISCUSSION

Figure 2 is a plot of the principal reduced conductivities (conductivity divided by the conductivity of the water phase) vs the ratio d/l for $\xi = 2.0$ and for (a) $v = 0.2$ and (b) $v = 0.4$. $k_\parallel$ is the conductivity along the cylinder axes, and $k_\perp$ is normal to the axes. As expected, both $k_\parallel$ and $k_\perp$ decrease as v increases. $k_\perp$ increases with increasing d/l while the variation of $k_\parallel$ is more complex. The same applies to Figure 3, which is a plot similar to Figure 2, but here $\xi = 0.2$. Comparing Figures 2 and 3, we note that $k_\perp$ decreases while $k_\parallel$ increases with increasing ξ. A qualitative justification of the above observations is illustrated by Figure 4, which is a z-section along the dashed line of Figure 1. i.e., along the diagonal of the unit cell, for $v = 0.3$ and various values of the parameters ξ and d/l. In drawing the cylinders, we kept the diameter the same in all cases, as the diameter of the

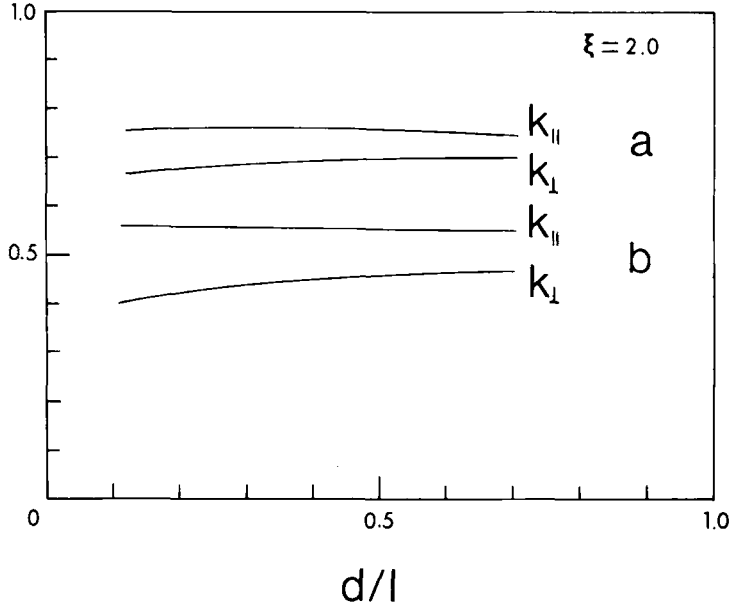

FIGURE 2 Principal values of the reduced conductivity vs the diameter to height ratio of the cylinders for $\xi = 2.0$; (a) for $v = 0.2$ and (b) for $v = 0.4$.

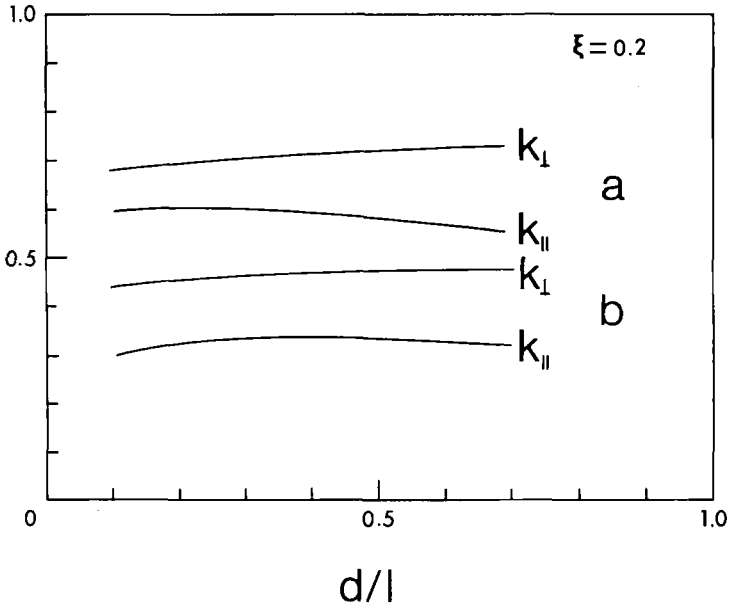

FIGURE 3 Principal values of the reduced conductivity vs the diameter to height ratio of the cylinders for $\xi = 0.2$; (a) for $v = 0.2$ and (b) for $v = 0.4$.

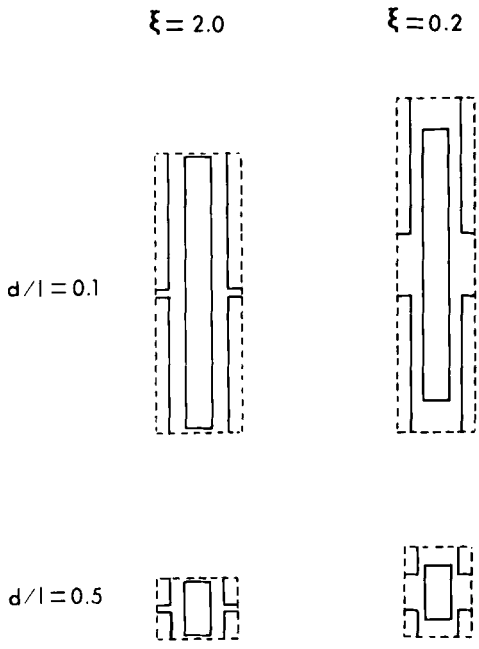

FIGURE 4 A z-section along the diagonal of the unit cell, for $v = 0.3$.

aggregates is about equal to twice the length of the amphiphilic molecule. We note that as ξ is increased (keeping v and d/l constant): (a) $h_\perp$ increases; and, (b) $h_\parallel$ decreases. As a direct consequence of (a) both $k_\parallel$ and $k_\perp$ increase, while in case (b) both conductivities decrease. One should then conclude that the dominant conduction for $k_\parallel$ is through the lateral gaps ($h_\perp$) and through the longitudinal gaps ($h_\parallel$) for $k_\perp$.

Next we introduce the conductivity anisotropy

$$\alpha = (k_\parallel - k_\perp)/(k_\parallel + k_\perp) \tag{1}$$

From Figures 2 and 3 we infer that in the range of concentrations considered here, α is small (less than 20%) and that the variation with d/l is accordingly slow. Choosing $d/l = 0.1$ we plotted α versus ξ in Figure 5, for (a) $v = 0.1$; (b) $v = 0.2$; (c) $v = 0.3$; and, (d) $v = 0.4$. For large ξ, α approaches the corresponding value obtained for infinitely long cylinders. These values, obtained from Ref. 2, are marked by a short line segment on the right hand side of the plot. For small ξ (less than 0.65–0.80) α is negative.

In connection with the N_c phase we are aware of two experimental measurements of the conductivity anisotropy. Gotz and Heckmann[5] used a velocity gradient to induce nematic order on an aqueous solution of

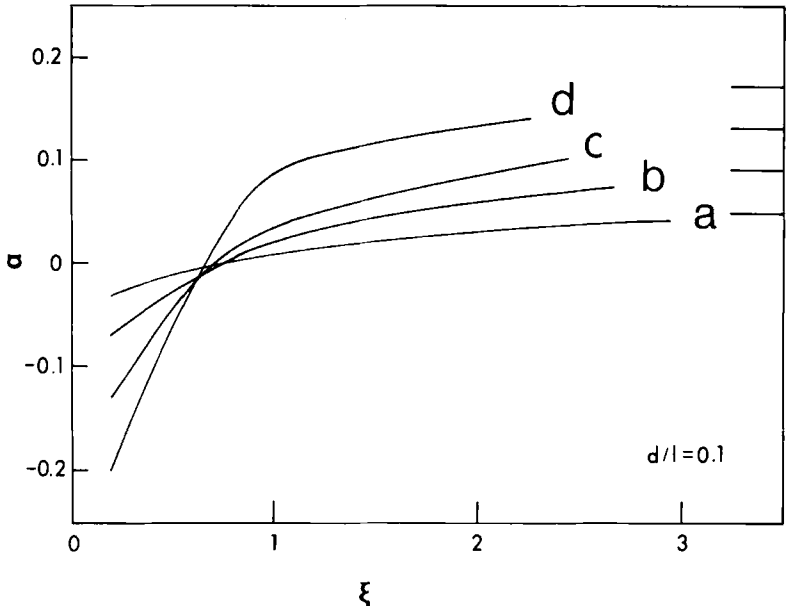

FIGURE 5 Anisotropy vs the ratio ξ for $d/l = 0.1$; (a) $v = 0.1$; (b) $v = 0.2$; (c) $v = 0.3$; and (d) $v = 0.4$. The values of α corresponding to a square arrangement of infinitely long cylinders are marked on the right hand side.

(19 wt.%) cetyltrimethylammonium bromide. The measured anisotropy was about 10% at 22°C. Burgar and Reeves[6] used a magnetic field to align a mixture of sodium decylsulfate/decanol/D_2O. They report negative conductivity anisotropy.

The model calculations presented above, predict both positive and negative values for the anisotropy. In geometric terms, the positive values result from small longitudinal ($h_{\|}$) spacing between the aggregates, while large $h_{\|}$ spacing will result into negative anisotropy.

In conclusion, it should be stated that we have essentially used a layered structure to which we added an intermediate layer between adjacent layers. Thus the model could overestimate $k_{\perp}$ (favor negative anisotropy). To determine the extent to which this happens, one would need to introduce additional intermediate layers, thus improving the approximation.

Acknowledgment

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